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A Novel Type of $[Mo_3O_9(L^*)]^{5-}$ Anion in the Structure of an Ammonium–Guanidinium Salt of a Mo^{VI} Complex with 1-Hydroxyethylidenediphosphonic Acid (H_4L)†

Vladimir S. Sergienko,*[a] Elena O. Tolkacheva,[a] Andrei B. Ilyukhin,[a] Zoya A. Starikova[b] and Inna A. Krol[b]

[a] *N. S. Karnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 117907 Moscow, Russian Federation. Fax: +7 095 954 1279*

[b] *The Scientific-industrial Union 'IREA', 107258 Moscow, Russian Federation.*

The synthesis and X-ray analysis of $(NH_4)_2[C(NH_2)_3]_3[MoO_3O_9(L^*)]\cdot 2.5H_2O$ have been carried out ($L^* = L^{5-}$); the trinuclear *anion has an unusual structure with a different number of terminal oxygen atoms in the 'yl' groups at the molybdenum* atoms (two MoO_2 groups and the MoO_3 group), where pairs of MoO_6 octahedra share a common face or vertex; the structure of the $[Mo_3O_9(L^*)]^{5-}$ anion is similar to that of one half of the $[Mo_6O_{17}(L_2^*)]^{8-}$ hexanuclear anion, in which the central bridging oxygen atom O_c is substituted by a terminal O_t.

The equilibria of complex formation by Mo^{VI} with H_4L in aqueous solutions for a system $M^+/H^+–MoO_4^{2-}–H_2L^{2-}$ [$M^+ = Na^+$, K^+, NH_4^+, $C(NH_2)_3^+$] can be represented by the general eqn. (1). ^{31}P NMR studies of systems with Mo:L = 3:1[1]

$$pH^+ + qMoO_4^{2-} + rH_2L^{2-} \rightleftharpoons (H^+)_p(MoO_4^{2-})_q(H_2L^{2-})_r \quad (1)$$

have shown that complex anions $(H^+)_p(MoO_4^{2-})_q(H_2L^{2-})_r$ having (p,q,r):$(10,6,2)^{6-}$, $(8,6,2)^{6-}$, $(8,6,2)^{8-}$, $(3.3.1)^{5-}$ and $(1,2,1)^{5-}$ are formed in concentrated aqueous solutions ($c_{Mo} = 0.5–1.0$ mol dm^{-3}). The selective influence of the outer sphere cation M^+ on the solubility of these complexes in the mixture was used to separate them by crystallization.[2] The structures of the crystal hydrates containing the complex anions (p,q,r):$(10,6,2)^{6-}$ $(NH_4)_6[Mo_6O_{17}(HL^*)_2]\cdot 10H_2O$,[3] $(8,6,2)^{8-}$ $K_8[Mo_6O_{17}(L^*)_2]\cdot 10H_2O$[1] and $(1,2,1)^{5-}$ $Na_5[Mo_2O_6L^*]\cdot 14H_2O$[4], $[C(NH_2)_3]_5[Mo_2O_6L^*]\cdot 3H_2O$[2] have been determined by X-ray analysis. These compound belong to the class of organic derivatives of heteropolymolybdates.[5]

In the present work the results of the synthesis of a novel complex $(NH_4)_2[C(NH_2)_3]_3[Mo_3O_9L^*]\cdot 2.5H_2O$ **1** with the anion $(3,3,1)^{5-}$ are given. The composition of complex **1** has been determined by X-ray analysis.‡ A new type of trinuclear polyanion, $[\{MoO_2(\mu_2\text{-}O)MoO_2(\mu_2\text{-}O)MoO_3\}(\mu_3\text{-}L^*)]^{5-}$, containing a neutral fragment Mo_3O_9 has been shown to constitute the basis of structure **1**.

$$(NH_4)_2[C(NH_2)_3]_3[Mo_3O_9L^*]\cdot 2.5H_2O$$

Single crystals of **1** were obtained by neutralization of an aqueous solution of system $NH_4^+/[C(NH_2)_3]^+–MoO_4^{2-}–H_2L^{2-}$ at M:L = 3:1 and pH ~ 6, which contained, as shown previously,[1,3] hexanuclear anions $[Mo_6O_{17}(HL^*)_2]^{6-}$ and $[Mo_6O_{17}L_2^*]^{8-}$. The neutralization equilibrium can be represented by eqn. (2).

$$[Mo_6O_{17}(HL^*)_2]^{6-} \xrightleftharpoons{2OH^-} [Mo_6O_{17}L_2^*]^{8-} \rightleftharpoons 2[Mo_3O_9L^*]^{5-} \quad (2)$$

Anion $[Mo_3O_9(L^*)]^{5-}$ in structure **1** [see Fig. 1(*a*)] lies in the crystallographic plane *m*, passing through all three molybdenum atoms, Mo(1–3), two bridging oxo-atoms O(2), O(4), terminal oxo-atom O(6) and atoms O(10), C(1) and C(2) of ligand L*. The latter functions as a pentadentate chelate-bridging ligand and is tridentate with respect to atom Mo(1) and bidentate with respect to atoms Mo(2) and Mo(3). Each

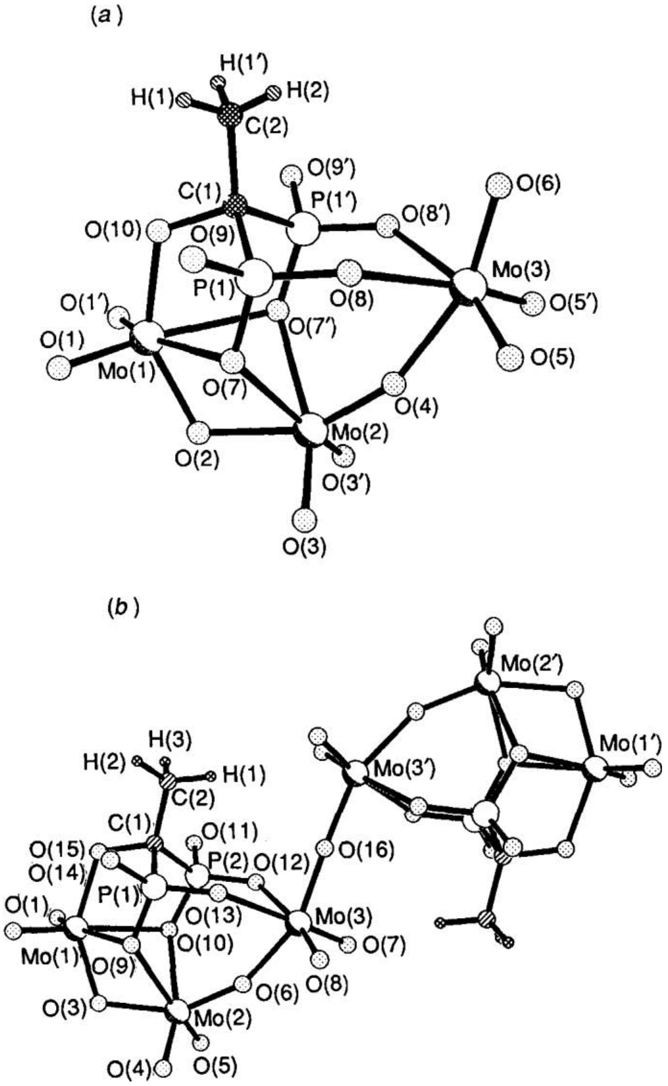

Fig. 1(*a*) The structure of trinuclear anion $[Mo_3O_9(L^*)]^{5-}$; interatomic bond lengths (Å) and angles (°): Mo(1)···Mo(2) 3.213(1), Mo(2)···Mo(3) 3.856(1), Mo(1)—O(1) 1.703(4), Mo(1)—O(2) 1.881(4), Mo(2)—O(2), 2.035(4), Mo(1)—O(7) 2.368(3), Mo(1)—O(10) 1.950 (4), Mo(2)—O(3) 1.724(4), Mo(2)—O(4) 1.769(4), Mo(2)—O(7) 2.320(3), Mo(3)—O(4) 2.152(4), Mo(3)—O(5) 1.737(4), Mo(3)—O(6) 1.751(5), Mo(3)—O(8) 2.243(3), P(1)—O(7) 1.554(3), P(1)—O(8) 1.529(3), P(1)—O(9) 1.507(3), P(1)—C(1) 1.837(4), O(10)—C(1) 1.443(7), C(1)—C(2) 1.512(9); Mo(1)—O(2)—Mo(2) 110.2(2), Mo(2)—O(4-)—Mo(3) 159.0(2), Mo(1)—O(7)—Mo(2) 86.4(1)
(*b*) Structure of the hexanuclear anion $[Mo_6O_{17}(L^*)_2]^{8-}$.

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† L* represents a ligand with a deprotonated aliphatic oxy-group.

‡ *Crystal data* for $Mo_3O_{16}P_2N_{11}C_5H_{29}\cdot 2.5H_2O$ **1**: orthorhombic, space group *Pnnm*, $a = 19.441(2)$, $b = 17.522(2)$, $c = 10.355(1)$ Å, $V = 3527.4(6)$ A^3, $Z = 4$, $D_x = 1.684$ g cm^{-3}, $\lambda(\text{Mo-K}\alpha) = 0.7107$ Å, $\mu(\text{Mo-K}\alpha) = 11.9$ cm^{-1}, $F(000) = 1780$, $M = 894$, $T = 296$ K. Intensity data were collected on a Enraf–Nonius CAD-4 diffractometer by the $\omega–2\theta$ scan method ($2\theta_{max} = 58°$). An empirical absorption correction was applied to the experimental data by the ψ-scanning method. The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques, isotropically for the water oxygen atoms and anisotropically for all other non-hydrogen atoms. The coordinates of the hydrogen atoms of the guanidinium cations and those of the methyl group were refined, while the thermal parameters of the hydrogens were assigned a fixed value. Final values of R and R_w are 0.0357 and 0.0414, respectively, for 3509 non-zero reflections with $I \geqslant 2\sigma(I)$. All calculations were performed on an IBM PC AT using SHELX 76 programs. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Centre. See Notice to Authors, *J. Chem. Soc., Chem. Commun.*, 1992, Issue No. 1.

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Table 1 Average bond lengths in the trinuclear complex $\mathrm{[Mo_3O_9(L^*)]^{5-}}$ **1** and hexanuclear species $\mathrm{[Mo_6O_{17}(L^*)_2]^{8-}}$ **2**, $\mathrm{[Mo_6O_{17}(HL^*)_2]^{6-}}$ **3** and $\mathrm{[Mo_6O_{17}(HL^*_{ap})_2]^{4-}}$ **4**[a]

Bond	**1**	**2**	**3**	**4**
Mo(3)—$\mathrm{O_c}$, [Mo(3)—$\mathrm{O_t}$]	1.751 ($\mathrm{O_t}$)	1.876 ($\mathrm{O_c}$)	1.878 ($\mathrm{O_c}$)	1.882 ($\mathrm{O_c}$)
Mo(3)—$\mathrm{O_b}$, *trans* to Mo(3)—$\mathrm{O_c}$ [Mo(3)—$\mathrm{O_t}$]	2.152	2.007	2.031	1.978
Mo(3)—$\mathrm{O_t}$	1.734*	1.717	1.706	1.711
Mo(1,2)—$\mathrm{O_t}$	1.713	1.713	1.713	1.714
Mo(1,2)—$\mathrm{O(P)_{chb}}$, *trans* to Mo(1,2)—$\mathrm{O_t}$	2.344	2.331	2.316	2.330
Mo(3)—$\mathrm{O(P)_{ch}}$, *trans* to Mo(3)—$\mathrm{O_t}$	2.243	2.218	2.223	2.221
Mo(1)—$\mathrm{O(C)_{ch}}$, *cis* to Mo(1)—$\mathrm{O_t}$	1.950	1.970	1.968	1.984
Mo(1)—$\mathrm{O_b}$, *cis* to Mo(1)—$\mathrm{O_t}$	1.881	1.875	1.892	1.875
Mo(2)—$\mathrm{O_b}$, *cis* to Mo(2)—$\mathrm{O_t}$	1.769; 2.035	1.841; 2.007	1.818; 2.031	1.855; 1.978

[a] The Mo(3)—O(6) bond [an 'analogue' of the Mo(3)—$\mathrm{O_c}$ bonds in structures **2–4**] was not taken into account.

Mo atom has a distorted octahedral coordination with two terminal oxo-atoms ($\mathrm{O_t}$) of the *cis*-dioxo-group and two O(P) atoms, of the two $\mathrm{PO_3}$ groups of ligand L*, *trans* to $\mathrm{O_t}$. The fifth and sixth positions in the $\mathrm{MoO_6}$ coordination octahedra are occupied by the bridging oxoatom $\mathrm{O_b}$ and by atom O(C) of the α-hydroxy group at Mo(1), two atoms $\mathrm{O_b}$ at Mo(2) and atoms $\mathrm{O_b}$ and $\mathrm{O_t}$ at Mo(3). Thus, the octahedra of the Mo(1) and Mo(2) atoms share a common face, and octahedra Mo(2) and Mo(3) a common vertex. The coordination sphere of the Mo(1,2) atoms contains two terminal oxygen atoms $\mathrm{O_t}$; the Mo(3) atom is coordinated to three $\mathrm{O_t}$ atoms. Such a type of trinuclear polyanion is unique for oxo complexes of $\mathrm{d^0}$ metals of groups 5–7, if the mode of the metal polyhedra sharing ('face + vertex') or 'yl'-groups with different numbers of terminal oxygen atoms in the same trinuclear complex ($\mathrm{MoO_2}$ and $\mathrm{MoO_3}$) is meant. In the structures of $\mathrm{Na_5[Mo_2O_6(L^*)]\cdot 14H_2O}$[4] and $\mathrm{[C(NH_2)_3]_5[Mo_2O_6(L^*)]\cdot 3H_2O}$[4,2] containing the binuclear anion $\mathrm{[Mo_2O_6(L^*)]^{5-}}$, di- and trioxogroups were found to be available simultaneously. On average, the Mo=$\mathrm{O_t}$ bonds in the $\mathrm{MoO_2}$ dioxo-groups are 0.027 Å shorter than those in the $\mathrm{MoO_3}$ trioxo-group (1.713 and 1.740 Å, respectively). The Mo—O bonds *trans* to Mo=O are, as usual, lengthened (to 2.152–2.368 Å) owing to the *trans*-effect of the multiply bonded oxo-ligands. An antibatic dependence between the lengths of Mo=$\mathrm{O_t}$ and Mo—$\mathrm{O_{trans}}$ is observed: the shorter the multiple Mo=O bond is, the longer the opposite Mo=$\mathrm{O_t}$ bond. Both oxo-bridges are asymmetrical; the difference between the lengths of the Mo(2)—$\mathrm{O(4)_b}$ and Mo(3)—$\mathrm{O(4)_b}$ bonds is 0.383 Å, while that between the Mo(1)—$\mathrm{O(2)_b}$ and Mo(2)—$\mathrm{O(2)_b}$ bonds is 0.154 Å.

In the L* ligands the bond P—O(7) to the oxygen atom bearing the chelate-bridging function ($\mathrm{O_{chb}}$) is longer than the P—O(8) bond to the chelating oxygen atom ($\mathrm{O_{ch}}$) [1.554(3) and 1.559(3) Å, respectively]. P—O(9) to the terminal oxygen atom [1.507(4) Å] is the shortest bond in structure **1**.

The trinuclear anion $\mathrm{[Mo_3O_9(L^*)]^{5-}}$ is genetically linked with the hexanuclear anion $\mathrm{[Mo_6O_{17}\{(\mathit{n}H)L^*\}_2]^{8-2\mathit{n}}}$ ($n = 0$)[4] [see Fig. 1(*b*)] and ($n = 1$)[3] and is derived from the latter by rupture of the central bridging bond Mo(3)—$\mathrm{O_c}$. In other words, trinuclear anion $\mathrm{[Mo_3O_9(L^*)]^{5-}}$ is one half of the $\mathrm{[Mo_6O_{17}\{(\mathit{n}H)L^*\}_2]^{8-2\mathit{n}}}$ hexanuclear anion; the only difference is that the bridging Mo(3)—$\mathrm{O_c}$ bond becomes a terminal one, Mo(3)—$\mathrm{O_t}$, and the 'yl' dioxo-group turns into the trioxo-group $\mathrm{Mo(O_t)_3}$ on passing to the trinuclear complex. A redistribution of the electron density over the $\mathrm{O_c(O_t)}$—Mo(3)—$\mathrm{O_b}$ (*trans*) [O(6)—Mo(3)—O)4)] axis occurs, followed by a shortening of the Mo(3)—$\mathrm{O_c}$ bond in the trinuclear complex [compared to the Mo(3)—$\mathrm{O_c}$ bond in the hexanuclear one] and a corresponding lengthening of the Mo—$\mathrm{O(4)_b}$ bond *trans* to Mo—$\mathrm{O_t}$.

Table 1 gives the average lengths of corresponding bonds in the structures of trinuclear anion $\mathrm{[Mo_3O_9(L^*)]^{5-}}$ **1**, hexanuclear species $\mathrm{[Mo_6O_{17}(L^*)_2]^{8-}}$ **2**,[1] $\mathrm{[Mo_6O_{17}(HL^*)_2]^{6-}}$ **3**[3] and $\mathrm{[Mo_6O_{17}(HL^*_{ap})_2]^{4-}}$ **4**[6] ($\mathrm{HL^*_{ap}}$ = hydroxy-γ-*N*,*N*-dimethylaminopropylidenediphosphonic acid). The Mo(3)—$\mathrm{O(6)_t}$ bond in the trinuclear anion is essentially shortened by 0.128 Å on average, compared with Mo(3)—$\mathrm{O_c}$ in the hexanuclear species (1.751 and 1.879 Å, respectively), while the opposite Mo(3)—$\mathrm{O(4)_b}$ bond is lengthened (by 0.147 Å) owing to the *trans*-effect of the multiply bonded oxo-ligand, from 2.005 Å (the average value for the three hexanuclear species **2–4**) to 2.152 Å in the trinuclear complex **1**. The two terminal bonds Mo–$\mathrm{O_t}$ at the Mo(3) atom are somewhat lengthened (by 0.023 Å on average, from 1.711 to 1.734 Å) compared with the hexanuclear species, which is to be expected on passing from the dioxo- to the trioxo-group. It should be noted that the Mo(1,2)—$\mathrm{O_t}$ bond lengths in the dioxo-groups of trinuclear anion **1** and those of the hexanuclear ones **2–4** are of equal length (1.713 Å).

Another difference between the geometric parameters of trinuclear anion **1** and the hexanuclear ones **2–4** is a shortening of the bridge bond length Mo(2)—$\mathrm{O_b}$ (by 0.063 Å on average, from 1.838 to 1.769 Å) and to a lesser degree (by 0.030 Å, from 2.005 to 2.035 Å) of the opposite Mo(2)—$\mathrm{O_b}$ bond *cis* to Mo—$\mathrm{O_t}$. One of the two Mo(2)—$\mathrm{O_b}$ bonds, Mo(2)—O(4) (1.769 Å), is shorter, while the other, Mo(2)—O(2) (2.035 Å), is longer than the two remaining Mo—$\mathrm{O_b}$ bridging bonds Mo—$\mathrm{O_b}$ *cis* to Mo=$\mathrm{O_t}$ in structure **1** [Mo(1)—O(2) 1.881 Å, Mo(1)—O(10) 1.950 Å], and one can therefore suggest a pseudo-trioxo-group $\mathrm{Mo(O_t)_2(O_b)}$ at the Mo(2) atom. An analogous pseudo-trioxogroup is available in one of two halves of the binuclear $\mathrm{[Mo_2O_6(L^*)]^{5-}}$ anion.[2,4]

The averaged values for the other corresponding metal—ligand bond lengths in trinuclear complex **1** on one hand, and those in the hexanuclear species **2–4** on the other, are close and differ by no more than 0.030 Å.

The complex anions and guanidinium cations in **1** are united by a branched system of ordinary and bifurcated N—H···O bonds, in which seven of the ten independent oxygen atoms of the anion [excluding $\mathrm{O(4)_b}$, $\mathrm{O(7)_{chb}}$ and $\mathrm{O(10)_{ch}}$] take part: N···O 2.877–3.070 Å, H···O 2.02–2.51 Å, NHO angles 113–173°. In **1** there are large cavities where an independent nitrogen atom of the ammonium cation, N(6), and three oxygen atoms, O(W1)–O(W3), are located. None of the latter positions corresponding to crystallization water molecules is fully populated [the population factors are 0.51(2), 0.42(2) and 0.33(2) for O(W1), O(W2) and O(W3),§ respectively].

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§ Such incomplete population results in unusually short distances O(W1)···O(W1) (1.89 Å) and O(W3)···O(W3) (1.90 Å) between the atom pairs related by the *m* plane for statistical positions of equal probability for O(W1) and O(W3).

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